

# PATENT SPECIFICATION

NO DRAWINGS

826.207



Date of Application and filing Complete Specification: July 22, 1957.

No. 23192/57.

Application made in Germany on July 23, 1956.

Complete Specification Published: Dec. 31, 1959.

Index at abstracts:—Class 2(4), P1(D1:D2:D3:D4:F5:F6), P9A4(A:B).

International Classification:—C09b.

## COMPLETE SPECIFICATION

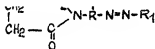
### *o-o'*-Dihydroxy-Monoazo Dyestuffs Containing Pyrrolidonyl Residues and their Metal Complex Compounds

SPECIFICATION NO. 826, 207

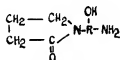
The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are Alfons Dörlars, of druckner-Strasse 7, Leverkusen, Germany and Otto Bayer, of Carl-Rumpff-Strasse 79, Leverkusen-Bayerwerk, Germany, both of German nationality.

THE PATENT OFFICE,  
7th March, 1960

DS 73112/1(6)/3930 200 3/60 DL



- 15 in which R stands for a radical of a diazo component of the benzene series and R<sub>1</sub> stands for a radical of a coupling component, R and R<sub>1</sub> bearing the hydroxyl group in *o*-position to the azo bridge.
- 20 The new monoazo dyestuffs are obtained according to the invention by combining diazo compounds of amines corresponding to the formula



- 25 wherein the amino- and the hydroxyl group stand in *o*-position to one another, with coupling components in *o*-position to a hydroxyl group.
- 30 The coupling process may be carried out in water or organic solvents, such as dimethyl formamide, in the presence of acid binding materials such as soda lye, ammonia, soda,
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according to conventional methods; for example by reacting aminophenols with  $\gamma$ -butyrolactone, nitrating the products thus obtained and subsequently converting the nitro group into an amino group.

As coupling components there may be used, for example, hydroxynaphthalenes and pyrazolones, such as 2-hydroxynaphthalene, 1-acetyl-7-hydroxynaphthalene, 1-methanesulfonylamino-7-hydroxynaphthalene, 2-acetyl-amino-6-hydroxynaphthalene, 4'-hydroxynaphtho-[2,1':4,5]-oxathiol-S-dioxide (naphthohydroquinone-methylene-sulphonether), 1-phenyl-3-methyl-5-pyrazolone and 1-(2'-chlorophenyl)-3-methyl-5-pyrazolone.

The metal-free monoazo dyestuffs are well suited for the dyeing of wool or wool-like materials according to the one-bath-chroming process, yielding dyeings of good fastness to light, good fastness to wear and tear, and good fastness to processing.

The metallization of the monoazo dyestuffs with chromium or cobalt in substance is carried out by processes described in literature, which according to experience produce the so-called 2:1-complexes, i.e. complexes which contain 2 molecules of dyestuff per metal atom. Suitable chroming processes are, for example, the

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Printed 25/59

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826,207



**Date of Application and filing Complete Specification:** July 22, 1957.

No. 23/92/57.

Application made in Germany on July 23, 1956.

**Complete Specification Published: Dec. 31, 1959.**

**Index at acceptance:—Class 2(4), P1(D1:D2:D3:D4:F5:F6), P9A4(A:B).**

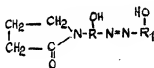
**International Classification:—C09b.**

## COMPLETE SPECIFICATION

***o-o'*-Dihydroxy-Monoazo Dyestuffs Containing Pyrrolidonyl Residues and their Metal Complex Compounds**

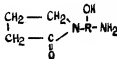
WE, FARBENFABRIKEN BAYER AKTIENGESSELLSCHAFT, a body corporate organised under the laws of Germany, of (22c) Leverkusen Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention comprises new monoazo dyestuffs, their chromium- and cobalt-complex compounds, and methods of making the same. The new monoazo dyestuffs of the invention correspond to the formula:



15 in which R stands for a radical of a diazo component of the benzene series and R<sub>1</sub> stands for a radical of a coupling component, R and R<sub>1</sub> bearing the hydroxyl group in *o*-position to the azo bridge.

20 The new monoazo dyestuffs are obtained according to the invention by combining diazo compounds of amines corresponding to the formula



25 wherein the amino- and the hydroxyl group stand in *o*-position to one another, with coupling components in *o*-position to a hydroxyl group.

30 The coupling process may be carried out in water or organic solvents, such as dimethylformamide, in the presence of acid binding materials such as soda lye, ammonia, soda,

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magnesium carbonate or pyridine.

As diazo compounds they may be used, for example, 2-amino-4-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-6-nitro-4-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-6-acetylamino-4-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-6-chloro-4-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-4-nitro-6-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-4-chloro-6-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-4-methyl-6-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene], 2-amino-6-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene]-4-methylsulphone, 2-amino-4-methyl-5-[[pyrroldiylidene-(1<sup>1</sup>)-1-hydroxybenzene]. These amines can be prepared according to conventional methods; for example by reacting aminophenols with  $\gamma$ -butyrolactone, nitrating the products thus obtained and subsequently converting the nitro group into an amino group.

As coupling components there may be used, for example, hydroxynaphthalenes and pyrazolones, such as 2-hydroxynaphthalene, 1-acetylmino-7-hydroxynaphthalene, 1-methanesulfonylamino-7-hydroxynaphthalene, 2-acetyl-amino-6-hydroxynaphthalene, 4<sup>th</sup>-hydroxynaphtho-[2,1':4,5]-oxathiol-S-dioxide (naphthothioquinone-methylene-sulphonether), 1-phenyl-3-methyl-5-pyrazolone and 1-(2'-chlorophenyl)-3-methyl-5-pyrazolone.

The metal-free monoazo dyestuffs are well suited for the dyeing of wool or wool-like materials according to the one-bath-chroming process, yielding dyeings of good fastness to light, good fastness to wear and tear, and good fastness to processing.

The metallization of the monoazo dyestuffs with chromium or cobalt in substance is carried out by processes described in literature, which according to experience produce the so-called 2:1-complexes, i.e. complexes which contain 2 molecules of dyestuff per metal atom. Suitable chroming processes are, for example, the

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reactions carried out in alkaline medium with chromium salicylic acid or with chromates in the presence of reducing carbohydrates, and suitable processes for treatment with cobalt are the reactions with bivalent or trivalent cobalt salts in alkaline medium.

It is also possible to react the chromium- or cobalt-yielding agents with two different dyestuffs according to the invention or with one according to the invention and the other being a known metallizable monoazo dyestuff. The mixed complexes thus formed may also be obtained in a pure form by producing first the 1:1 complexes (1 atom of chromium or cobalt per one molecule of dyestuff) and by reacting the complexes thus obtained with a further molecule of a metal-free dyestuff to form the 2:1-complexes.

The dyestuff chromium- and cobalt- complexes are slightly soluble in water. They are suitable for the dyeing of resins, lacquers and plastic masses, but they are more preferably used for the printing and dyeing of materials of animal origin such as leather, wool and silk. Also dyeings produced therewith on synthetic fibres such as polyamide and polyurethane fibres show very good fastness properties. The chromium- and cobalt- complex dyestuffs dye wool from a neutral to weakly acid bath and yield dyeings of very good fastness properties.

The following Examples are given for the purpose of illustrating the invention:—

#### EXAMPLE 1.

a) 19.3 g. of 2-amino-4-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxybenzene are dissolved with 125 ml. of water and 20 ml. of hydrochloric acid ( $d = 1.18$ ) and diazotized with 35 ml. of a 20 per cent. sodium nitrite solution while stirring and cooling with ice. The suspension of the diazo compound is run at 5 to 10° C. into a solution of 14.5 g. of 2-hydroxynaphthalene, 15 ml. of 40 per cent. soda lye and 25 g. of dry soda in 400 ml. of water. After the coupling is complete the monoazo dyestuff is precipitated with the addition of rock salt and filtered with suction.

b) The wet paste is suspended in 1.5 l. of water diluted with the addition of 20 ml. of 40 per cent. soda lye, heated to 85° C. and treated dropwise with stirring at 85–90° C. with a solution of 9 g. of potassium bichromate and 10 g. of glucose in 100 ml. of water. After metallization is finished the chromium complex compound thus obtained is salted out, isolated and dried. It represents a dark blue powder which dyes wool from a neutral to weakly acid bath in level reddish dark-blue shades of very good light and wet fastness.

c) The dyestuff paste obtained according to 1 a) is dissolved in 2 litres of water with 6 g. of sodium hydroxide. At 90° C. there is added dropwise with stirring a solution which has been prepared as follows:

15 g. of crystalline cobalt sulphate are dis-

solved in the cold in 250 ml. of water; this solution is poured with vigorous stirring into 150 ml. of a 25 per cent. ammonia solution and then treated with 5 ml. of 30 per cent. hydrogen peroxide.

The cobalting is completed immediately after having dropwise added the cobalt solution into the alkaline solution of the dyestuff. After cooling to 60° C. the cobalt-containing dyestuff is precipitated by adding 500 g. of rock salt and 50 g. of sodium bicarbonate, and isolated. A dark powder is thus obtained which dyes wool from a neutral bath in very level bluish bordo shades having very good light—and wet fastness.

The diazo component used in this Example may be prepared by reacting 4-aminophenol with  $\gamma$ -butyrolactone, mono-nitrating and reducing the 2-nitro-4-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxybenzene thus obtained. The 2-amino-4-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxybenzene is separated in form of colourless crystals which have a melting point of 168 to 169° C.

#### EXAMPLE 2.

21 g. of 2-amino-4-methyl-6-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxy-benzene are diazotized in a usual manner with 6.9 g. of sodium nitrite, and combined with a solution of 30.5 g. of the sodium salt of 1-acetyl-amino-7-hydroxynaphthalene-3-sulphonic acid, 15 ml. of 40 per cent. soda lye and 25 g. of dry soda in 350 ml. of water. When the coupling is complete the monoazo dyestuff thus obtained is salted out. After drying it represents a dark blue powder which dyes wool after-chromed in reddish navy blue shades of good fastness properties.

The 2-amino-4-methyl-6-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxy-benzene used in this Example as diazo component can be obtained by nitrating 4-methyl-6-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxybenzene and reducing the 2-nitro compound thus obtained; the product crystallizes in weakly yellowish needles having a melting point of 113–114° C.

#### EXAMPLE 3.

23.7 g. of 2-amino-6-nitro-4-[pyrrolidonyl-(1<sup>1</sup>)]-1-hydroxybenzene are diazotized in a usual manner in aqueous hydrochloric acid solution. The suspension of the diazo compound is run at 5–10° C. into a solution of 20.5 g. of 1-acetyl-amino-7-hydroxynaphthalene, 20 g. of dry soda and 20 ml. of 40 per cent. soda lye in 350 ml. of water. The coupling is complete after a short period. The paste of the isolated dyestuff is suspended in 1.6 l. of water and the dyestuff converted into the chromium complex compound according to the instructions given in Example 1b.

After drying, the chromium-containing dyestuff represents a black powder which dissolves in water with a dark blue colouration and which dyes wool from a neutral or weakly acid bath in somewhat greenish dark blue shades of very good fastness to light and to wetting.

The diazo component used in this Example is obtainable by dinitrating 4-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene and partial reduction of the 2,6-dinitro-4-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene thus obtained. The product is isolated in dark red prisms of a melting point of 178 to 179° C.

#### EXAMPLE 4.

23 g. of 2-amino-4-chloro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene are diazotized in a usual manner with 6.9 g. of sodium nitrite. The diazo salt solution is slowly poured into a solution of 24 g. of 4'-hydroxynaphtho-[2,1':4,5]-oxathiol-S-dioxide (naphthohydroquinone-methylene-sulphonether, obtainable according to the method described and claimed in U.K. Specification No. 731,495) in 220 ml. of water and 30 ml. of 40 per cent. soda lye. After completion of the coupling the dyestuff thus obtained is filtered with suction and dried. The dyestuff dissolves in dilute soda lye with a deep blue colouration and dyes wool by the monochrome-process in navy blue shades of very good fastness to light, fastness to wetting and fastness to processing.

2-Amino-4-chloro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene can be obtained by reacting 2-amino-4-chloro-1-hydroxybenzene with  $\gamma$ -butyrolactone, nitrating and reducing the nitro group of the 2-nitro-4-chloro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene thus obtained. The product is isolated in form of colourless needles having a melting point of 142 to 143° C.

#### EXAMPLE 5.

23.7 g. of 2-amino-4-nitro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene are dissolved in hydrochloric acid medium and combined with stirring at 5° C. with a solution of 21 g. of 1-(2'-chlorophenyl)-3-methyl-5-pyrazolone, 8 ml. of 40 per cent. soda lye and 20 g. of dry soda in 500 ml. of water. After the coupling is complete the monoazo dyestuff thus formed is salted out and filtered.

The wet dyestuff paste is suspended in 1.2 l. of water and 18 ml. of 40 per cent. soda lye and treated dropwise at 90° C. while stirring with a solution of 7.5 g. of sodium bichromate and 10 g. of glucose in 100 ml. of water. The chromium complex compound is salted out. After drying it represents a dark red powder which dyes wool from a neutral to a weakly acid bath in level bluish red shades having very good fastness properties.

The 2-amino-4-nitro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene can be prepared as follows: 2-amino-1-hydroxybenzene is reacted with  $\gamma$ -butyrolactone. The resulting product is dinitrated and the 2,4-dinitro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene thus obtained is partially reduced. One obtains olive green crystals with a melting point of 186 to 188° C.

#### EXAMPLE 6.

21 g. of 2-amino-4-methyl-5-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene are diazotized. The

diazo salt solution is added, while stirring, at 5 to 10° C. to a solution of 20.5 g. of 2-acetylmino-6-hydroxynaphthalene, 25 g. of dry soda and 20 ml. of 40 per cent. soda lye in 350 ml. of water. After the coupling has been finished the precipitation of the dyestuff is completed by adding rock salt.

The wet dyestuff paste is suspended in 1.4 l. of water and the dyestuff converted into its chromium complex compound according to the method described in Example 1b. After drying, the chromium-containing monoazo dyestuff represents a black powder which dyes wool from a weakly acid bath in level greenish grey shades of very good fastness properties.

2-Amino-4-methyl-5-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene can be produced by reacting 3-amino-4-methyl-1-hydroxybenzene with  $\gamma$ -butyrolactone, nitrating and reducing the 2-nitro-4-methyl-5-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene. Colourless needles are thus obtained.

#### EXAMPLE 7.

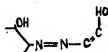
19.3 g. of 2-amino-5-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene are diazotized and coupled with 17.5 g. of 1-phenyl-3-methyl-5-pyrazolone. The monoazo dyestuff thus obtained is converted into the cobalt complex compound according to the instructions given in Example 1c. A dark red powder is thus obtained which dyes wool from a natural bath in level strong orange brown shades, having very good fastness properties.

By using 25.6 g. of aceto-acetic acid-(3-sulphonamidophenyl)-amide instead of 1-phenyl-3-methyl-5-pyrazolone and proceeding in an analogous manner to that described above a brown red powder is obtained which dyes wool from a weakly acid bath in yellowish brown shades with very good fastness properties.

#### EXAMPLE 8.

23 g. of 2-amino-4-chloro-6-[pyrrolidonyl-(1<sup>3</sup>)]-1-hydroxybenzene are diazotized and combined with 23.7 g. of 1-methane-sulphonyl-amino-7-hydroxynaphthalene. The chromium complex of this monoazo dyestuff which is obtained according to the instructions given in Example 1b dyes wool from a weakly acid bath in very level slightly greenish grey shades of very good fastness properties.

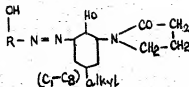
In U.K. Patent Specification No. 637,404, there are described and claimed a process, and the products thereof, for the manufacture of metalliferous dyestuffs free from sulphonic acid groups by the action of agents yielding metal upon azo-dyestuffs which are free from sulphonic acid groups and from carboxylic acid groups standing in the ortho-position to hydroxyl groups and which contain the atomic grouping



wherein the treatment with the agent yielding metal is conducted in a neutral to alkaline medium and the aforesaid agent is a metal compound which contains an aromatic ortho-oxy-carboxylic acid in complex union, and with the use of a proportion of the complexforming metal corresponding to less than one atom for each group in the dyestuff capable of leading to the formation of complexes.

In U.K. Patent Specification No. 758,016, we have described and claimed a process of making chromiferous dyestuffs which consists in mixing a dyestuff containing at least one group which can be chromed, with a chromate and a reducing carbohydrate in an alkaline medium.

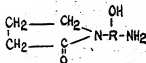
In U.K. Patent Specification No. 776,318, we have described and claimed new monoazo dyestuffs corresponding to the general formula:



Wherein R stands for a radical of the benzene series, free from sulphonic and carboxylic acid groups and bearing the hydroxy group in *o*-position to the  $-\text{N}=\text{N}-$  bridge; and the metal complex compounds thereof.

#### WHAT WE CLAIM IS:—

1. Methods of producing new monoazo dyestuffs by combining diazo compounds of amines corresponding to the formula

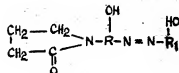


wherein R stands for a radical of the benzene series and wherein the amino- and the hydroxy group stand in *o*-position to one another, with coupling components in *o*-position to a hydroxyl group.

2. Methods according to claim 1 in which the diazo compounds and the coupling components are any of those hereinbefore specified.

3. Methods of producing new monoazo dyestuffs and their chromium- and cobalt-complex compounds, substantially as described in any of the foregoing Examples.

4. Monoazo dyestuffs, when obtained according to the methods of any of Claims 1 to 3, corresponding to the formula:



wherein R stands for a radical of a diazo component of the benzene series and R<sub>1</sub> means a radical of a coupling component, R and R<sub>1</sub> bearing the hydroxyl group in *o*-position to the azo bridge.

5. Chromium- and Cobalt- complex compounds of monoazo dyestuffs according to Claim 4 when the dyestuffs are obtained according to the methods of any of Claims 1 to 3.

6. The monoazo dyestuffs, when prepared according to the methods of any of Claims 1 to 3, and their chromium and cobalt complex compounds, according to claim 4 and claim 5, respectively, which are described in the foregoing Examples.

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